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Dinitrogen Reduction by a Chromium(0) Complex Supported by a 16-Membered Phosphorus Macrocycle

Michael T. Mock,*,[‡] Shentan Chen,[‡] Molly O'Hagan,[‡] Roger Rousseau,[‡] William G. Dougherty,[†] W. Scott Kassel,[†] and R. Morris Bullock[‡]

[‡]Center for Molecular Electrocatalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, United States

[†]Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085, United States

Supporting Information

ABSTRACT: We report a rare example of a Cr−N_2 complex supported by a 16-membered phosphorus macrocycle containing pendant amine bases. Reactivity with acid afforded hydrazinium and ammonium, representing the first example of N_2 reduction by a Cr−N_2 complex. Computational analysis examined the thermodynamically favored protonation steps of N_2 reduction with Cr leading to the formation of hydrazine.

Group 6 Mo and W dinitrogen complexes supported by phosphine ligands have been extensively studied in the context of the reduction of N_2 to ammonia at a single metal center.[1] Moreover, the identification of N_2 intermediates leading to the stoichiometric production of hydrazine and ammonia in these systems, upon protonation by acids, furthered our understanding of the N_2 reduction pathway, as a means to help interpret biological N_2 fixation by the nitrogenase enzymes.[2] Only two catalytic, homogeneous systems have achieved N_2 reduction under mild conditions using protons and electrons;[3] both are Mo-based complexes. While Mo and W form robust "Chatt-type"[1b] ($(P-P)_2M(N_2)_2$, P−P = diphosphine ligand) complexes, Cr−N_2 complexes are often thermally unstable,[4] thus, with very few exceptions[5] are rarely isolated. Therefore, their reactivity patterns with acid are unknown.

Macrocyclic[6] and linear[7] (poly)phosphine ligands have received increasing attention due to enhanced kinetic and thermal stability of their metal complexes. This stability is especially important in systems for N_2 reduction in which the ligand is required to support a range of metal oxidation states. We are interested in utilizing ligand sets that contain pendant bases to facilitate proton movement and modulate redox potential upon protonation[8] for N_2 reduction. Bidentate ligands [8]-$P^R{}_2N^{R'}{}_2$ (substituted 1,5-diaza-3,7-diphosphacyclooctanes) have served as scaffolds for Ni-based H_2 oxidation and production catalysts[9] and in systems designed for O_2[10] and N_2[5a] reduction. Herein, we report the formation of 12- and 16-membered phosphorus macrocycles, containing pendant amine bases, and the formation of hydrazine and ammonia from the protonation of a Cr−N_2 complex (with the electrons coming from Cr), supported by a 16-membered macrocycle. These results illustrate the first example of N_2 reduction by a chromium dinitrogen complex[11] and identifies Cr as a candidate for the development of a catalytic N_2 reduction system.

We previously reported the synthesis of (κ^3-$P^{Ph}{}_2N^{Bn}{}_2$)$CrCl_3$ from the reaction of $CrCl_3(THF)_3$ and $P^{Ph}{}_2N^{Bn}{}_2$ and conversion to *cis*-$[Cr(N_2)_2(P^{Ph}{}_2N^{Bn}{}_2)_2]$ by reduction with Mg under N_2 in the presence $P^{Ph}{}_2N^{Bn}{}_2$.[5a] As an alternative to preparing the Cr(0)−N_2 complex from a Cr(III) precursor, our synthetic efforts focused on the target complex $CrCl_2(P^{Ph}{}_2N^{Bn}{}_2)_2$. Addition of $CrCl_2(THF)$ to a THF solution of 2 equiv of [8]-$P^{Ph}{}_2N^{Bn}{}_2$ resulted in a bright-green solution that slowly turned brown after 2 h. The desired $CrCl_2(P^{Ph}{}_2N^{Bn}{}_2)_2$ was not isolated. Purification led to the isolation of two Cr products (Scheme 1), both of which contained expanded macrocyclic rings as newly formed ligands.[12]

Dark-blue crystals of the Cr(III) complex *fac*-$[CrCl_3(P^{Ph}{}_3N^{Bn}{}_3)]$ (**1(Cl)**$_3$) were isolated in 25% yield. The crystal structure, (Figure 1) shows the expansion of the [8]-$P^{Ph}{}_2N^{Bn}{}_2$ ligand into a 12-membered macrocycle, [12]-$P^{Ph}{}_3N^{Bn}{}_3$. The second Cr-containing product, isolated as dark-yellow crystals in (reproducible) 5% yield, was identified as *trans*-$[CrCl_2(P^{Ph}{}_4N^{Bn}{}_4)]$ (**2(Cl)**$_2$) bearing a 16-membered macrocycle, [16]-$P^{Ph}{}_4N^{Bn}{}_4$ (Scheme 1; see Supporting Information (SI) for X-ray structure). Stereochemistry of the phenyl groups in **2(Cl)**$_2$ indicates the all-*syn*-isomer of the [16]-$P^{Ph}{}_4N^{Bn}{}_4$ ligand, which is the major isomer produced in this reaction. Red crystals of the *syn*−*anti*−*anti*-isomer of *trans*-$[CrCl_2(P^{Ph}{}_4N^{Bn}{}_4)]$ were identified crystallographically (see SI). Mechanistic details have not been elucidated for this remarkable ligand rearrangement, in which an 8-membered ring gives 12- and 16-membered rings. Cr(II) halides have been shown to participate in C−C bond-forming and P−C bond-cleavage reactions,[13] and thus, we propose that Cr is involved in the formation of the larger macrocycle products.

Reduction of a suspension of **2(Cl)**$_2$ with Mg powder in THF under N_2 (1 atm) affords *trans*-$[Cr(N_2)_2(P^{Ph}{}_4N^{Bn}{}_4)]$ (**2(N**$_2$**)**$_2$) in 63% yield. A singlet at δ 40.1 in the $^{31}P\{^1H\}$ NMR spectrum (THF-d_8) indicates four equivalent phosphorus nuclei. IR data (THF) exhibit an intense ν_{NN} band at 1918 cm^{-1} and a weak band at 2072 cm^{-1}, assigned as the

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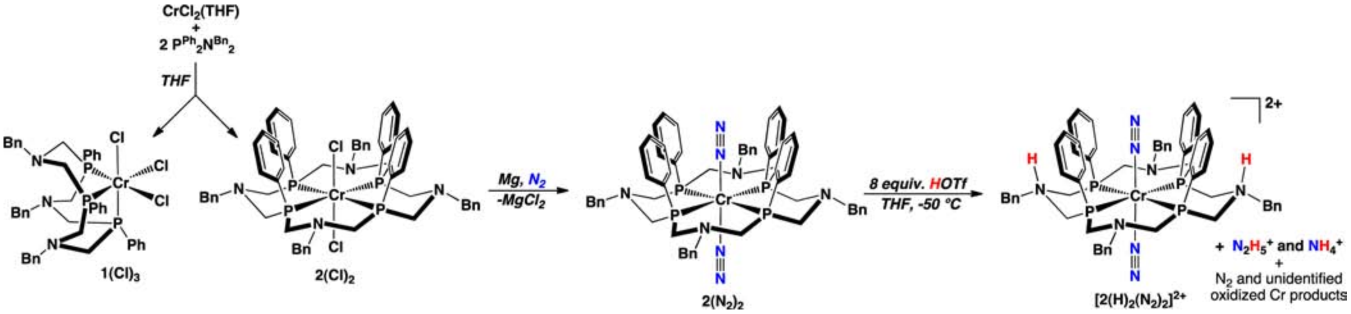
Scheme 1



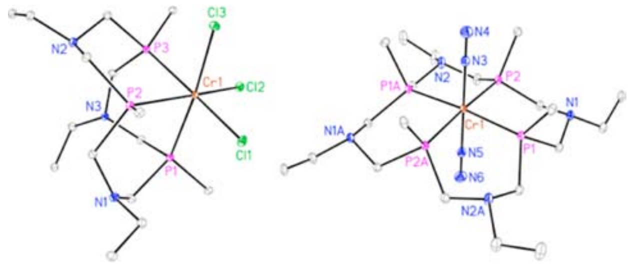


Figure 1. Molecular structures of *fac*-$[CrCl_3(P^{Ph}{}_3N^{Bn}{}_3)]$ **1(Cl)**$_3$, (left) and the all-*syn*-isomer of *trans*-$[Cr(N_2)_2(P^{Ph}{}_4N^{Bn}{}_4)]$ (**2(N**$_2$**)**$_2$), (right). Only the ipso carbons of the phenyl and ipso and methylene carbons on the benzyl groups are shown. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 30% probability.

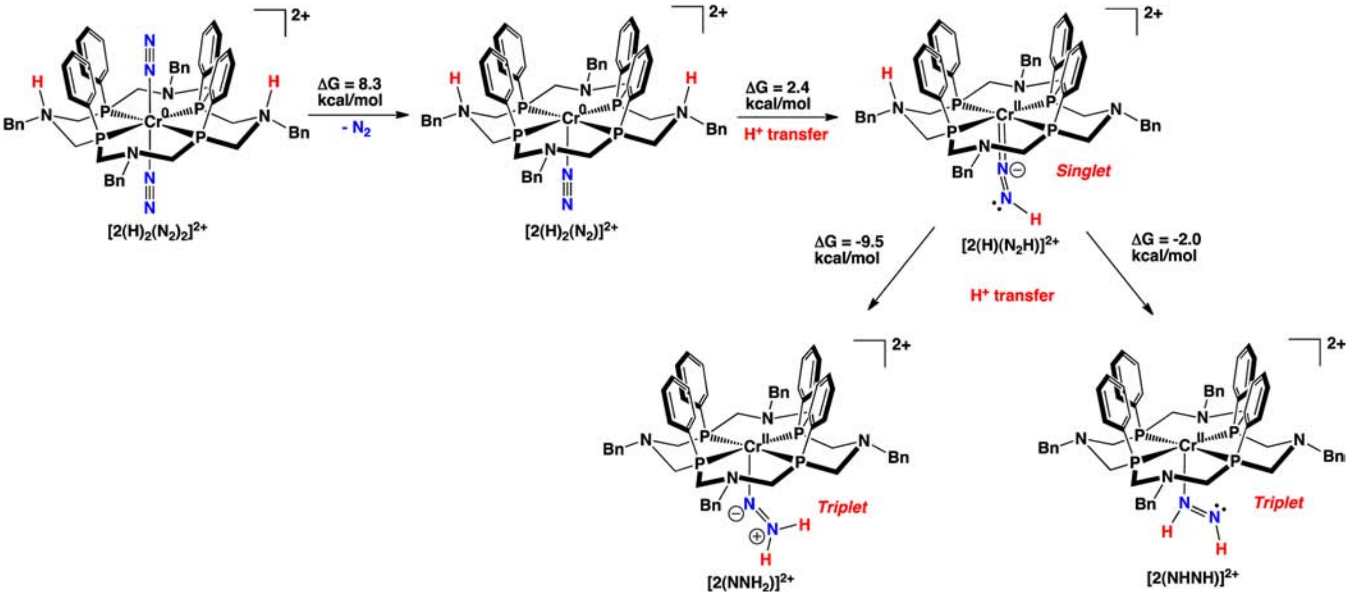
antisymmetric and symmetric ν_{NN} stretching modes, respectively. Samples prepared with $^{15}N_2$ exhibit ν_{NN} bands shifted to lower energy at 1855 and 2003 cm^{-1}. Crystallographic analysis of **2(N**$_2$**)**$_2$ reveals an octahedral Cr center within the equatorial plane of four phosphorus atoms, with a Cr−P bond length of 2.2676(4) Å and all-*syn*-phenyl groups on the phosphorus atoms, Figure 1. The phenyl groups create a "pocket", occupied by an axial N_2 ligand (atoms N3−N4). Four chelate 6-membered rings in the chair conformation contain pendant amine lone pairs *syn* to the phenyl substituents. Metric parameters about the axial N_2 ligands reflect the contrasting steric environment above and below the equatorial plane. The bond length of Cr1−N3 is 1.930 (2) Å, and that of N3−N4 is 1.112(3) Å, whereas the opposing "out of pocket" N_2 ligand has a shorter Cr−N bond (Cr1−N5 = 1.884(2), and that of N5−N6 is 1.120(3) Å. Density functional theory (DFT)-based electronic structure calculations, which reproduce the asymmetry of the two bound N_2 units, suggest the electron-rich environment in the pocket destabilizes the Cr−N binding[5a] of the "in pocket" N_2 ligand leading to a dissociation energy of only 11 kcal/mol compared to 18 kcal/mol for the "out of pocket" N_2 (see SI for details).

Treatment of **2(**^{15}**N**$_2$**)**$_2$ in THF-*d*$_8$ with triflic acid (HOTf) was monitored by NMR spectroscopy. Addition of HOTf at 25 °C resulted in immediate loss of the coordinated N_2 and phosphine ligand, and produced no reduced N_2 products; thus, the reactions were performed at low temperature. Upon addition of 3 equiv of HOTf, initial ^{31}P NMR data (−50 °C) showed the appearance of two new products in a ∼2:1 ratio:[14] a singlet at δ 47.9 and peaks of equal intensity at δ 49.4 and 37.5, assigned as $[Cr(^{15}N_2)_2(P^{Ph}{}_4N^{Bn}{}_4H_2)]^{2+}$ ($[\mathbf{2(H)_2(N_2)_2}]^{2+}$) and $[Cr(^{15}N_2)_2(P^{Ph}{}_4N^{Bn}{}_4H)]^{+}$ ($[\mathbf{2(H)(N_2)_2}]^{+}$), respectively. Upfield resonances indicative of P_4N_4 ligand loss from the metal were also observed. No evidence of a Cr−H was present in the ^1H NMR spectrum. While focusing on the protonated ^{15}N-containing products originating from the $^{15}N_2$ ligands (only labeled intermediates and products are detected in the ^{15}N NMR experiments), after 5 h a cross-peak was observed in the $^1H-^{15}N$ HSQC spectrum with a ^{15}N chemical shift at δ −181.0, correlating to ^1H signal at δ 12.1. These data support the tentative assignment of the $N_\beta{}^{15}$ of a diazenido[16] species ($Cr-^{15}N_\alpha-^{15}N_\beta-H$), the first protonation step in the reduction of N_2. For comparison, *trans*-$[WBr(^{15}N_2H)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) exhibits ^{15}N chemical shifts of $^{15}N_\alpha$ at −25.9, N_β at −187.1.[17] The $^{15}N\{^1H\}$ NMR spectrum contained multiple ^{15}N resonances in the region δ −15 to −42 (and free $^{15}N_2$ at δ −71), corresponding to Cr bound $^{15}N_2$ ligands in $[\mathbf{2(H)(^{15}N_2)_2}]^{+}$ and $[\mathbf{2(H)_2(^{15}N_2)_2}]^{2+}$. Free hydrazinium ($^{15}N_2H_5{}^+$)[18] was first detected in the ^{15}N NMR spectrum after 27 h as a singlet at δ −329 (^1H cross-peak at δ 10.8 in $^1H-^{15}N$ HSQC; $J^{15}{}_{N-H}$ = 75 Hz), indicating reduction of the $^{15}N_2$ ligand. Treatment of this sample with an additional 5 equiv of HOTf at −50 °C immediately affords $[\mathbf{2(H)_2(^{15}N_2)_2}]^{2+}$ at δ 47.9 in the ^{31}P NMR spectrum and four resonances at δ −18, −23 −32, and −40 in the $^{15}N\{^1H\}$ NMR spectrum for two Cr-bound $^{15}N_2$ ligands. Over the next 18 h the resonance for free $^{15}N_2H_5{}^+$ became more intense, and a resonance appeared at δ −364 (cross-peak at δ 7.0 in $^1H-^{15}N$ HSQC spectrum) indicating trace $^{15}NH_4{}^+$ formation[19] (see SI). The final oxidized Cr-containing products were not identified.

Electronic structure methods were employed to augment the protonation studies of **2(N**$_2$**)**$_2$ to interrogate the initial protonation steps leading to hydrazine formation (Scheme 2; see SI for full details). Protonation of the amine site(s) is favored over N_2 in accordance with formation of $[\mathbf{2(H)_2(N_2)_2}]^{2+}$. Protonation of the P_4N_4 ligand lowers the "in pocket" $Cr-N_2$ dissociation free energy by ∼2 kcal/mol per protonation, thus, making N_2 labile even at −50 °C. Dissociation of N_2 effects the basicity of the remaining coordinated N_2 ligand, raising its proton affinity by ∼12 kcal/mol, which is important for proton transfer to occur from a pendant amine,[20] in $[\mathbf{2(H)_2(N_2)}]^{2+}$ as shown in Scheme 2, to form a diazenido species, $[\mathbf{2(H)(N_2H)}]^{2+}$, which is ∼2 kcal/mol higher in energy than $[\mathbf{2(H)_2(N_2)}]^{2+}$. This species is thus thermally populated in a ratio of ∼10^{-2} at −50 °C in accord with the low concentration of diazenido species observed in the $^1H-^{15}N$ HSQC spectrum. Theoretical simulations suggest the diazenido ligand is slightly nonlinear, (Cr−N−N = 168°; Cr−N = 1.65 Å; N−N = 1.23 Å).

A second proton transfer from the protonated pendant amine is thermodynamically favored at the proximal or distal nitrogen atom, forming a diazene[21] $[\mathbf{2(NHNH)}]^{2+}$ or a hydrazido $[\mathbf{2(NNH_2)}]^{2+}$ intermediate, respectively. While the

Scheme 2



hydrazido species was found to be the lower-energy product, in both pathways the Cr center undergoes a spin-state change from singlet to triplet, with the triplet spin-state being lower in energy by ~8 kcal/mol. A spin-state transition is expected to be slow as it is symmetry forbidden. Simulations indicate a bent hydrazido ligand (Cr−N−N = 144°; N−N = 1.30 Å) and a Cr−N bond length of 1.73 Å, indicative of primarily Cr−N single bond character. This structure contrasts with typical Mo and W hydrazido complexes that contain a linear $M-N-NH_2$ linkage, due to multiple metal−nitrogen bonding. On the basis of the bonding description of the Cr-hydrazido species, further proton addition steps are postulated to occur at the proximal nitrogen atom, keeping the N−N bond intact en route to hydrazine formation. Furthermore, DFT results suggest triflate binding to higher oxidation states of Cr promotes the dissociation of the reduced N_2 product and possible P_4N_4 ligand loss.

In summary, a $Cr-N_2$ complex supported by a unique 16-member phosphorus macrocycle has been characterized. This work demonstrates the first example where Cr activates coordinated N_2, with the addition of acid affording hydrazinium ($^{15}N_2H_5^+$) (electrons originating from Cr) as the major reduced $^{15}N_2$ product. Computational analysis predicts the reduced $Cr-N_2$ intermediates do not exhibit Cr−N multiple bonding. The implications of this bonding description, due to the Cr spin-state,[22] influence the N_2 reduction pathway, leading to hydrazine formation. Ongoing studies are aimed at controlling the movement of protons to facilitate the formation of reduced N_2 products, and probing the reactivity of this compound with reducing agents for the catalytic production of hydrazine and/or ammonia.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details and data, X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

michael.mock@pnnl.gov

Notes

The authors declare no competing financial interest.

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(11) A hydrazido species, ($Cr(NNH_2)$), was suggested from IR data in ref 5b.

(12) The mass balance of this reaction consisted of unreacted 8-[$P^{Ph}{}_2N^{Bn}{}_2$] and $CrCl_2(THF)$ in addition to unidentified free ^{31}P-containing products (possible ligand fragments).

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(14) The ratio of $[\mathbf{2}(\mathbf{H})_2(\mathbf{N}_2)_2]^{2+}$ to $[\mathbf{2}(\mathbf{H})(\mathbf{N}_2)_2]^{+}$ slowly changes over 72 h to ~1:2.

(15) N_α is expected to be in the region −15 to −45 in the ^{15}N spectrum and could not be identified among the resonances of the Cr-bound $^{15}N_2$ ligands.

(16) Diazenido ligands have been identifed to exhibit a ^{15}N chemical shift in this region of the spectrum, distinguishing them from species such as hydrazido ligands, see ref 17.

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(18) Hydrazinium triflate was prepared and characterized independently; see Supporting Information for details.

(19) (a) Qualitatively, hydrazinium is clearly the major reduced $^{15}N_2$ product as found by ^{15}N NMR. Trace ammonium formation could be attributed to hydrazinium decomposition, see Schmidt, E. *Hydrazine and Its Derivatives: Preparation, Properties and Applications*; Wiley-Interscience: New York, 1984.

(20) A proton from acid in solution could not be ruled out; however, this leads to formation of a tricationic species.

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